A Study on the Sintering of Ultrafine Grained Tungsten with Ti-Based Additives

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Abstract

Tungsten (W) is a brittle material at room temperature making it very difficult to fabricate. Although the lack of ductility remains a difficult challenge, nano-sized and ultrafine grain (UFG) microstructures offer potential for overcoming tungsten's room temperature brittleness. One way to manufacture UFG W is to compact and sinter nanosized W powder, however, it is a non-trivial task to control grain growth during sintering. In an effort to inhibit grain growth, the effect of Ti-based additives on the densification and grain growth of nano-W powders was investigated in this study. The addition of 1 wt.% Ti into tungsten led to more than a 63% decrease in average grain size of sintered samples at comparable density levels. It was also found that sintering in Ar yielded a finer grain size than sintering in H₂ at similar densities. Compared to conventional high temperature sintering, a lower temperature sintering cycle for a longer hold time resulted in both near-full density and fine grain size. The roles of the Ti additive include not only the inhibition of grain growth, but also the potential absorption of oxygen from W particles.

Keywords: Nanocrystalline Material, Tungsten, Titanium, Sintering, Grain Growth, Ultrafine Grain

1. Introduction

Tungsten is a remarkable structural metal, and is used in a range of demanding environments and applications, such as light bulb filaments, heating elements and turbine components. Tungsten is also the principle proposed material for plasma facing components in fusion reactors [1-2]. However, issues with brittleness at room temperature along with a high ductile-brittle transition temperature (DBTT) cause serious reservations concerning its use in fusion reactors and restrict its use in other demanding applications [3-4]. In addition, tungsten recrystallizes at temperatures much lower than its melting point, a microstructural effect that tends to cause intergranular brittleness [5]. The development of tungsten alloys with improved mechanical properties, particularly at elevated temperatures, is important to several industries, and in terms of fusion reactor applications, could have profound consequences for society at large.

The development of tungsten alloys with very small grains, ultrafine-grains or nano-grains, has been approached as a route to improve the ductility and decrease the DBTT, since the large fraction of grain boundaries in the ultrafine-grained microstructure could shift the deformation mechanism [6]. Y.

Kitsunai et al. demonstrated a significant decrease of the DBTT in ultrafine grained tungsten with an average grain size of 0.44 μm [7]. Other BCC metals, including Al and Mo, have been shown to exhibit improvements in ductility and DBTT by forming nanocrystalline structures [8-9]. In ultrafine grained materials the increased grain boundary area has been seen to decrease the impurity concentration at grain boundaries [10-11]. In the case of tungsten, a decrease in grain boundary impurities could lead to improved strength and toughness.

In order to manufacture ultrafine grained tungsten, two general methods have been investigated: the top-down and the bottom-up approaches [11]. Severe plastic deformation (SPD) based techniques are the most often used top-down approach, and have shown improvement in the strength and toughness of tungsten [12-14]. However, this approach is often impractical from a manufacturing perspective due to problematic scale-up combined with the fact that this approach cannot be used to fabricate shapes with complex geometries. Alternately, the bottom-up approach involves the synthesis of nano-W powders, compaction of the nano powder, and a powder metallurgy (PM) approach involves compaction and sintering of powders. The control of grain growth during sintering is the greatest obstacle in the bottom-up PM method. Sintering W of more conventional grain sizes employs temperatures above 2,000 C, and the grain size of tungsten can reach 18 μm , or greater, with a sintered density less than 95% [15].

Several authors have investigated other techniques, such as hot isostatic pressing (HIP), microwave sintering or spark plasma sintering (SPS), in order to obtain ultrafine-grained tungsten via the bottom-up approach [16-18]. A study by M. Monge et al. reported the consolidation of pure W with an average grain size of 4.4 μm by using a HIPing technique, and obtained a relative density of 92.7% [16]. Another research group obtained an average grain size of 3.2 μm using microwave sintering of pure W, but with a relative density of 96.9% [19]. Homogeneous dispersion of thermally stable particles, like La_2O_3 and Y_2O_3 , have been used in W microstructures as an effective means to retain fine W grain size by inhibiting grain boundary migration during sintering [10, 19]. Y. Kim et al. reported near fully dense W – 5% Y_2O_3 with an average grain size of 3.7 μm by spark plasma sintering at 1700 C [20]. The addition of 5 wt.% Y_2O_3 to tungsten, however, reduced the theoretical density from 19.25 g/cm^3 to less than 16.85 g/cm^3 . Another research team has successfully produced W -1% Y_2O_3 samples with 99% density and an average grain size of 3.2 μm by spark plasma sintering at 1800 C [21]. The grain size obtained, 3.2 μm , is much larger than the ultrafine grain range, which is generally defined as less than 500 nm. The manufacture of near fully dense tungsten material with high density and ultrafine grain size remains a technical challenge.

Titanium carbide, TiC, another thermally stable particle has also been used to inhibit grain growth in tungsten. As reported by X. Ding et al., spark plasma sintering of W – 1%TiC produced an average grain size of 3 μm and relative density of 98.6% [22]. Additionally, S. Lang et al. demonstrated a decrease in tungsten's DBTT to below 300°C on samples that had undergone hot rolling with an 83% reduction ratio of sintered W-TiC alloy [23]. Theoretical and experimental research on the alloying of tungsten with Ti metal, as well as work on other Ti compounds, have also shown sufficient cause for further investigation. First principles simulations performed by D. Jiang suggested the ductility of bcc W could be improved by the addition of Ti [24]. Research on W-Ti oxide dispersion strengthened alloys with low Ti additive compositions by C. Chen et al., showed uniform microstructures, but as the content of Ti increases to 10%, the microstructure becomes non-uniform [25]. And, S. Wang et al. reported on the spark plasma sintering of a TiN reinforced W-Ti alloy, which reached a very high density with a 0.62 μm average grain

size using a Ti composition of 4% [26]. Despite these diverse and promising Ti alloy studies, the effect of Ti additives on tungsten sintering is still lacking.

Many researchers have predicted the difficulty of consolidating nano tungsten powders to achieve full density, while maintaining ultrafine grain size. It has generally been held that ultrahigh compaction pressure and very low sintering temperature are necessary [27, 28]. In contrast, however, research by Wang et al. showed it is possible to sinter nano-W powders to near-full density at relatively low sintering temperatures, using pressureless sintering techniques [29, 30]. The potential of using additive dispersion to further assist in producing fine grain size using the pressureless low temperature sintering of nano-W powders was deemed advantageous.

In the present work, a detailed investigation was undertaken of the low temperature pressureless sintering of milled nano-W powders with Ti-based additives. The effect of Ti-based additives on the grain growth of nano-W is presented, and a method to further minimize final grain sizes by adjusting sintering process parameters is discussed. The ultimate goal of this work is to manufacture ultrafine-grained tungsten by using a conventional pressureless sintering process, through optimizing processing parameters, including the use of nano-sized W powder, low sintering temperatures, and the use of Ti as a grain growth inhibitor.

2. Experimental Procedure

Feedstock materials were procured from commercial vendors, and included: tungsten, titanium hydride and titanium carbide powders. The tungsten powders had an average particle size of approximately 50 nm, and the Ti and TiC powders each were approximately 44 μm . The powders were further milled using a custom designed high-energy planetary ball mill (HEPM) [31] for 6 h in a mixture of heptane and ethanol. The ball to powder ratio was 5:1. The 60 g-force acceleration field generated during the planetary ball milling effectively reduced the tungsten and Ti powders to the nano-scale. The average grain size of milled powders was characterized as 17 nm using an x-ray diffraction line broadening technique. Details of the milling process have been described previously [32].

Green parts were formed from the milled W-Ti powders by compacting into 16 mm diameter cylinders using a uniaxial die press with 54 MPa pressure and a 5 min hold time. The average green density was measured at 6.29 g/cm³, which is approximately 34% of the relative density. The reduction and sintering processes of the compacted green parts were performed using an atmosphere controlled tube furnace. All samples were reduced at 700 °C for 3 h with flowing H₂ to remove the oxide that formed on tungsten powders during the milling and drying processes. After reduction, the samples were sintered at 1000 to 1300 °C for 1 to 16 h in either flowing Ar or H₂ to study the effects of sintering temperature, atmosphere, and time on the grain coarsening and densification behaviors of the nano-W-Ti powders.

The Archimedes method was used to measure the density of sintered samples. Samples were then mounted in epoxy resin and polished using diamond suspensions to a 0.25 μm surface finish. Grain size measurements were made from SEM micrographs of polished surfaces using a strong backscattered component that revealed grain orientation contrast. Average grain sizes were determined using the linear intercept method. At least 400 intercepts of grains were measured from at least 5 randomly

selected SEM images for each sample. The average grain sizes were calculated based on the lengths of these intercepts. To study the chemical states of tungsten and titanium of the sintered W -1%Ti samples, samples were fractured using a hand-held shear cutter inside a glove box under Ar atmosphere, in order to obtain fresh fracture surfaces without oxidation. These samples were transferred into a Kratos Axis Ultra x-ray photoelectron spectroscopy (XPS) system, using an atmosphere controlled stage, and XPS spectra were taken on the fresh fracture surfaces. Subsequently, fracture surfaces of sintered samples were characterized using an FEI NovaNano scanning electron microscope (SEM), and the chemical compositions of different phases were analyzed using the energy-dispersive X-ray spectroscopy (EDS) method. TEM samples were fabricated by the focused ion beam technique, and analyzed in a JEOL JEM-2800 equipped with EDS and dual tilt stage. The bulk oxygen contents of sintered samples were characterized using a LECO TCH600 N/O/H determinator.

3. Results and Discussion

3.1 Effects of the Ti Additive on Sintering of Nano-W Powders

To study the effects of Ti additions on grain growth and densification, a range of compositions was investigated, alloying nano-W with 0-3 wt.% of either TiC or Ti. Regarding Ti, titanium hydride was the initial feedstock, but the hydrogen disassociates during heating to the reduction/sintering temperatures. TiH₂ is not stable at high temperature, and Ar, of course, is inert, so little difference would be anticipated between the two atmospheres. Figure 1 shows the change of relative sintering density as a function of additive composition for the nano-W powder prepared using HEPM processing with Ti or TiC. Samples of Figure 1 and 2 were sintered first at 1050 °C for 2 h and then at 1300 °C for 1h in hydrogen atmosphere. The sintering density of nano-W powders decreases as the Ti or TiC composition increases, and a 3 wt.% addition of TiC leads to approximately a 20% decrease in the relative density. Compared to TiC, the Ti additive leads to a much more gradual decrease in sintered density as the additive composition increases, and is able to reach 94% relative density with a composition of 3 wt.%.

Figure 1 Effects of Ti and TiC composition on the relative sintering density of HEPM milled nano-W powders.

The key objective of adding Ti to UFG or nano-W in the present work is to reduce grain growth during sintering through grain boundary pinning. Figure 2 shows a grain size vs. relative density plot of nano-W powders with 0 to 3 wt.% Ti. The 1 wt.% Ti addition led to a dramatic decrease in the average grain size of sintered nano-W powders from 1,572 nm to 577 nm. Further increases in Ti composition up to 3 wt.% led to no significant change in the average grain size. However, the addition of Ti also decreased sintered density under the same sintering conditions, and increasing Ti content showed decreasing final density. These results indicate that the addition of Ti inhibits both grain growth and densification during the sintering process. Comparing the relative density and grain size results, the Ti addition reached its maximum effect as a grain growth inhibitor at, or below, 1 wt.%, but its effect on impeding densification continued to increase as the Ti composition increased. Larger amounts of the Ti additive, with its lower density, also led to significant decreases in the theoretical density of the nano-W material, which is undesired for many applications. Therefore, W with 1 wt.% Ti additive was the optimal composition within the parameters of this study, providing refined grain size with relatively high sintering density. The remainder of this study focuses solely on the addition of Ti.

Figure 2 Grain size vs. relative sintered density of nano-W powder with different Ti additive compositions.

3.2 Effect of Temperature and Atmosphere on Sintering of Nano-W Powder with Ti Additive

Sintering was performed in either argon or hydrogen environments to examine potential differences in sintering kinetics. Figure 3 compares the relative density change as a function of sintering temperature with H₂ or Ar atmosphere for the nano-W powders with 1% Ti. In both atmospheres, the sintering density of the W – 1% Ti samples increases as the sintering temperature increases. In the hydrogen atmosphere, W -1% Ti samples sintered at 1000 °C for 1 h showed limited densification, and only marginally exceeded 90% density at 1100 and 1200 °C. The maximum density for the H₂ atmosphere was 93.95%, which resulted from sintering at 1300 °C for 1 h. Sintering W – 1% Ti in an Ar atmosphere led to improved densification; a relative density of 92% was reached with a temperature as low as 1100 °C. The highest density of 98.28% was obtained by sintering at 1300 °C for 1 h. As reported in earlier work, this low temperature sintering approach is only achievable by using nano-sized tungsten powders [32]. The better densification in Ar atmosphere is likely due to enhanced bulk-diffusion and limited vapor transportation, as WO₂(OH)₂ may be minimized during sintering [32].

Figure 3 Effect of temperature and atmosphere on the relative sintering density of nano-W powders with 1 wt.% Ti.

To augment data measurements on densification and grain growth of nano-W powders with Ti alloying, microstructures of W-1% Ti samples were examined that had been sintered with H₂ and Ar atmospheres across a range of temperatures. SEM images of the surfaces of W – 1% Ti samples that were fractured by impact are shown in Fig. 4. The W–1% Ti powders sintered at 1000 °C in H₂, Fig. 4a, showed the least densification of the samples examined. The fracture surface is very similar to a compacted green part, with only slightly larger particle size and a smoother surface. Compared to the sample sintered at 1000 °C, the samples sintered at 1100 and 1200 °C in H₂ exhibited bonding, which began to form between particles, and some grains showed a polyhedral morphology. There is still significant porosity, but some channels are divided into smaller segments, and open porosity appears to be diminished. Samples sintered at 1300 °C for 1 h in H₂ showed a more consistent polyhedral morphology, Fig. 4d, with fewer interconnected pores. This corresponds to an intermediate to final stage of sintering.

In contrast to samples sintered in a H₂ atmosphere, W -1% Ti samples sintered in Ar had much lower porosity, combined with W grains that exhibited a more classically polyhedral shape. The microstructure of a sample sintered at 1000 °C in Ar, Fig. 4e, begins to show the formation of bonds between grains. Sintering at 1100 °C and above exhibited a clear increase in grain size, along with isolated spheroidal pores, which corresponds to the final stage of sintering. As sintering temperature was increased, improved densification was observed along with increased grain size, and a small number of spherical pores can still be observed at grain boundaries even when sintered at 1300 °C. This analysis of the sintered microstructures is consistent with the reported density results, since at equivalent temperature, sintering in Ar always resulted in better densification than sintering in H₂. While 1300 °C was necessary for the H₂ sintered sample to reach greater than 90% density, the Ar sintered samples reached 92% relative density at only 1100 °C.

Figure 4 SEM fracture surfaces of sintered nano-W with 1 wt.% Ti additive at: (a) 1000 °C in H₂, (b) 1100 °C in H₂, (c) 1200 °C in H₂, (d) 1300 °C in H₂, (e) 1000 °C in Ar, (f) 1100 °C in Ar, (g) 1200 °C in Ar and (h) 1300 °C in Ar.

The variation of average grain size, measured on polished cross sections, as a function of relative density for W-1%Ti samples is given in Fig. 5. The average grain size increases as the sintering temperature and relative density increase (see also Fig. 3). The grain size of samples sintered in a H₂ atmosphere increases gradually as the sintering temperature and relative density increase, and reaches 600 nm at 1300 °C with 93.95% relative density. Similarly, the grain size of Ar atmosphere sintered samples also increases slowly as the sintering temperature increases up to 1100 °C, and relative density reaches 92%. However, for sintering temperatures above 1100 °C the improved density leads to rapid grain growth, and the average grain size reaches 1010 nm at 1300 °C. The rapid grain coarsening effect becomes active during the final stage of sintering. Within this data set, to reach an equivalent relative density, sintering in Ar always required much lower sintering temperature and led to a much finer grain size than sintering in H₂.

Figure 5 W grain size vs. relative density of nano-W powder with 1 wt.% Ti additive sintered at different temperatures and under argon or hydrogen atmospheres.

The scaling law can be used to describe the relationship between grain size and sintering behavior for W powders sintered in Ar or H₂ atmospheres, and is given by the following equation [33-35]:

$$n \ln \left(\frac{d_1}{d_2} \right) = \frac{Q}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

Here, d_1 and d_2 are the grain sizes at two different sintering temperatures, T_1 and T_2 are those corresponding sintering temperatures, Q is the activation energy, and R is the ideal gas constant (8.314 J/mol*k). The constant, n , is an exponent dependent on active diffusion mechanisms; where $n = 0.67$ for vapor transport, $n = 0.5$ for volume diffusion and $n = 0.33$ for grain boundary diffusion. German et al. [36] calculated the Q/R value of tungsten sintering, and using empirical evidence reported it to be 4407 K. Based on previous studies and data obtained in this work, the relationships between sintering temperature and grain size in Ar and H₂ atmospheres were examined, Fig. 6 (a) and (b). Figure 6 (a) shows the sintering behavior of nano-W powders with Ti in an Ar atmosphere, falling between the curves for volume diffusion and grain boundary diffusion. A best-fit curve provides an excellent match to the experimental data with an n value equal to 0.38. In this case, all samples sintered quickly to greater than 90 % relative density, Fig. 3, thus allowing easy comparison of the data in terms of grain size analysis. Therefore, the dominant mechanism for densification in the sintering of nano-W powder with Ti in an Ar atmosphere is likely a mixture of volume diffusion and grain boundary diffusion.

As opposed to sintering in Ar, sintering in an H₂ atmosphere led to a more complex behavior. Figure 6 (b) shows that in the low temperature range, the data matches well with the calculated curve for vapor transport. With increasing temperature, the experimental results begin to shift, and obtain an excellent fit with the calculated volume diffusion curve for temperatures above 1200 °C. This result is consistent with our previously reported research, where in a H₂ atmosphere, tungsten experienced chemical vapor transport as a result of the volatile WO₂(OH)₂ phase [32]. At higher sintering temperatures, the efficient reduction of WO₂ results, and WO₂(OH)₂ is not as prevalent. The disparity in fit of the data in Fig. 6(b) may be due to differences observed in densification rate across the tested temperature range.

Figure 6 Relationship of sintering temperature and grain size described by the scaling law for nano-W with 1 wt.% Ti sintered in an (a) Ar and (b) H₂ atmosphere.

3.3 Effect of Time on Sintering of Nano-W Powders

As discussed in the previous section, in order to avoid the rapid grain coarsening caused by high temperature sintering, a relatively low sintering temperature, near 1100 °C or lower, is required. However, a 200 °C drop in sintering temperature leads to a significant decrease in densification kinetics. To obtain sintered W samples with high density and fine grain size in the present work, ultra long sintering times were employed to overcome the limitation of densification kinetics at low temperature. Nano-W powders with a 1% Ti additive were sintered at 1100 °C in Ar atmosphere for times ranging from 1 to 16 h, and Fig. 7 shows a plot of relative density vs. sintering time. Based on the figure, increasing the sintering time from 1 to 16 h leads to a substantial increase in sintering density, from 92.27% to 96.70%. This density is comparable to the sintering density obtained from higher temperature sintering at 1200 to 1300 °C. The rate of densification decreases as the sintering time and density increases, but nonetheless makes a significant improvement during the 8 to 16 h period. The average grain sizes of these low-temperature sintered samples were characterized using SEM, and the results are shown in Fig. 8. Generally, the grain size of sintered samples increased as the relative density increased. However, only 205 nm of growth was observed on the average grain size as the density increased from 92.27% to 96.7%, which is much less than a comparable density result obtained by increasing the sintering temperature. Furthermore, no trend for rapid grain coarsening is observed on the plot even when the sintering density increases above 93%, where grain growth was seen to rapidly increase in this system at higher temperatures. The result of this sintering cycle, using extended time at low temperature, demonstrates a potential approach to obtaining ultrafine grain sizes in tungsten with near-full density, while maintaining limited grain growth.

Figure 7 Relative density vs. sintering time of nano-W powders with Ti during sintering at 1100 °C in Ar atmosphere.

Figure 8 W grain size vs. relative density for W-1wt.% Ti samples sintered at 1100 °C from 1 to 16 h in Ar atmosphere.

3.4 Grain Growth Inhibition and Oxygen Absorption Effects

Based on discussion above, the addition of Ti leads to a dramatic decrease in the average grain size of sintered nano-W powders over pure W samples. Figure 9 shows an SEM micrograph of the fracture surface of a W-1 wt.% Ti sample sintered at 1300 °C. The lighter gray phase is the sintered tungsten matrix, and the darker phase is the Ti rich second phase (note: some pull out of the latter phase can be observed). Intergranular fracture was dominant in this fracture surface, with cracks propagating principally along the grain boundaries and phase boundaries; so, the cohesive strength of these boundaries is much lower than that of the W grains. The Ti rich phase was homogeneously distributed in the tungsten samples, and was observed to primarily be located along grain boundaries in polished cross sections. The average grain size of the Ti particles was approximately 290 nm with a generally spherical shape, and the Ti grain size was much smaller than the 1010 nm average grain size for tungsten. It is known that well dispersed thermally stable oxide particles, like Y_2O_3 , can hinder grain boundary migration and inhibit grain growth, which may improve strength and high temperature stability [18]. For

W -1 wt.% Ti material, the Ti may also work as a grain growth inhibitor in a similar manner, explaining the significant decrease seen in the average grain size in UFG tungsten with the addition of Ti.

Figure 9 Fracture surface showing microstructure of W -1 wt.% Ti sample sintered at 1300 °C under Ar atmosphere.

To obtain more accurate information about the chemical states of Ti and W in sintered samples, XPS measurements were performed on a fresh fracture surface without exposure to oxygen. Figure 10 (a) and (b) show the spectra of Ti 2p and W 4f peaks from the XPS analysis. The position of the primary W peak is located at 31.3 eV, which is the typical energy range for metallic tungsten [37]. Taking the large energy difference between tungsten and tungsten oxide into consideration, the peak profiles of the W 4f peaks indicate this sample mainly contains tungsten in its metallic state. The position of Ti 2p peaks are shifted toward a higher energy, and are located at 459 eV, which is the typical energy range for the TiO_2 state [37]. No signal is observable at the 454 eV position for metallic titanium. Therefore, the near surface of the Ti phase is essentially TiO_2 .

Figure 10 XPS analysis of fresh fracture surfaces of sintered ultrafine grained W – 1 wt% Ti sample. (a) W 4f peaks and (b) Ti 2p peaks.

There are two stages during processing where the Ti additive may become oxidized. This can occur during the milling and drying stage, where Ti may be exposed to oxygen in the air, or during the reduction and sintering stage, where Ti may function as a reducing agent for W oxide. To further understand the oxidation of Ti within the bulk of sintered samples, oxygen contents of the sintered samples were characterized using a LECO N/O/H determinator. Figure 11 compares the O content

obtained in this manner with the theoretical estimated O contents for sintered W powders with different Ti compositions. The theoretical estimated O content is calculated based on the assumption of all Ti additives having been fully oxidized. Based on the figure, oxygen content increases linearly as the Ti composition increases. The experimental O content is always less than the estimated O content, which indicates partial oxidation of Ti, with metallic Ti likely remaining at the core of these particles. If the Ti oxidation happens solely during the milling and drying processes, due to the abundant amount of O in the air, all the Ti particles should be oxidized to the same saturated level. In this case, the ratio between experimental O and estimated O should be constant for all Ti compositions. However, this ratio decreases as the Ti composition increases, which is about 0.78 for 1% Ti, 0.73 for 2% Ti and 0.69 for 3% Ti. This indicates the involvement of the reduction/sintering processes in the Ti oxidation. The decrease of this ratio with increasing Ti content can be understood such that only a limited amount of the Ti need be oxidized as a reducing agent, and the percentage of Ti thus oxidized will decrease as the total amount of Ti additive increases. Alternately, the partial oxidation of the Ti phase may be the result of passivation or partial oxidation of near surface regions of any given Ti particle.

Figure 11 Comparison of experimental bulk O content measurements and estimated O content (full TiO₂) of sintered nano-W powders with different Ti compositions.

Transmission electron microscopy (TEM) was used to gain further information on the Ti rich phase in the microstructure. Figure 12 shows a bright field micrograph of a typical Ti rich phase within the microstructure and very near the thin edge of the TEM foil. Qualitative EDS analyses of Ti rich particles showed the presence of minor amounts of Cr, V and Fe, which may have been scavenged from the milling container. Analysis by EDS of circular regions in Fig. 12, marked A and B, showed a profound difference in the titanium to oxygen contents of the two regions. Area A, presumably thicker given that it is further from the edge of the TEM foil, showed a ratio of the Ti K-alpha peak height to O K-alpha peak height of ~1.4, while area B, the thinner region of the foil, showed a ratio of 0.89. This data corroborates the XPS findings and oxygen content data of Fig. 11, and indicates that while the near surfaces oxidize readily, there is likely metallic Ti in the interior of these particles.

Figure 12 TEM bright field micrograph of a Ti rich phase in nano-W-1%Ti

The Ti within bulk sintered W may not only function as a grain growth inhibitor, but may also function as a reducing agent, absorbing oxygen from the surrounding W grains and grain boundaries during the reduction and sintering process. In addition to the reduction effect of the hydrogen atmosphere during processing, this oxygen absorption behavior may help to further reduce the oxygen level of the W grains and grain boundaries. Tungsten is known to be sensitive to oxygen contamination, as a minor amount of oxygen can increase the activation energy for surface diffusion during sintering [38], and oxygen segregating to grain boundaries can decrease the grain boundary cohesion [10]. Therefore, this oxygen absorption behavior of Ti may be particularly valuable, as it could improve both the sintering of W and also the strength and toughness of sintered materials.

4. Conclusions

Addition of minor amounts of Ti to the high energy planetary milled nano-tungsten powders inhibited the grain growth during sintering, and led to a dramatic decrease in the average grain size of sintered ultrafine-grained W samples. Compared to a H_2 atmosphere, W -1% Ti nano-powders sintered in Ar showed improved densification with less grain growth. Long duration low temperature sintering was shown to be an effective method to obtain samples with near-full density and refined grain size, compared to higher temperature sintering. SEM and XPS studies showed that the Ti addition not only functioned as a grain growth inhibitor, but may also absorb oxygen from adjacent W grains or grain boundaries.

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